

** cooling from
cholesteric to
smectic phase*

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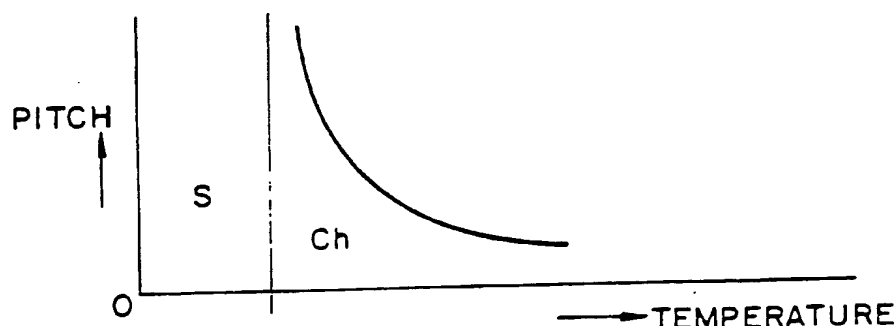
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EP 0136725 A EP 0092181 A EP 0091637 A
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(54) **Smectic liquid crystal devices**

(57) A method, device, and material for providing a fast switching liquid crystal display employs the ferro electric effect of chiral smectic liquid crystal material. To provide a uniform appearance the liquid crystal material is arranged to have a long cholesteric pitch at a temperature close to a smectic/cholesteric phase transition temperature. This long cholesteric pitch allows liquid crystal molecules to cool from the cholesteric to smectic phase with a uniform alignment. The smectic material is contained in a cell between walls (2, 3) bearing electrodes (5, 6) and surface treated to provided homogeneous alignment of liquid crystal material (7).



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<p>(21) International Application Number: PCT/GB87/00222 (22) International Filing Date: 1 April 1987 (01.04.87) (31) Priority Application Number: 8608114 (32) Priority Date: 3 April 1986 (03.04.86) (33) Priority Country: GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW1A 2HB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : BRADSHAW, Madeline, Joan [GB/GB]; Underleaf, Upleadon, Gloucestershire GL18 1EJ (GB). RAYNES, Edward, Peter [GB/GB]; 25 Leadon Road, Hall Green, Malvern, Worcestershire (GB).</p>		<p>(74) Agent: BECKHAM, Robert, William; Procurement Executive, Ministry of Defence, Patents 1A(4), Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: SMECTIC LIQUID CRYSTAL DEVICES</p> <div data-bbox="422 1192 1307 1533"> </div> <p>(57) Abstract</p> <p>A method, device, and material for providing a fast switching liquid crystal display employs the ferro electric effect of chiral smectic liquid crystal material. To provide a uniform appearance the liquid crystal material is arranged to have a long cholesteric pitch at a temperature close to a smectic/cholesteric phase transition temperature. This long cholesteric pitch allows liquid crystal molecules to cool from the cholesteric to smectic phase with a uniform alignment. The smectic material is contained in a cell between walls (2, 3) bearing electrodes (5, 6) and surface treated to provide homogeneous alignment of liquid crystal material (7).</p>		

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SMECTIC LIQUID CRYSTAL DEVICES

The invention relates to smectic liquid crystal devices.

Liquid crystal devices commonly comprise a thin layer of a liquid crystal material contained between two glass plates or walls. A
5 thin transparent electrode is deposited on the inner face of both walls. The combination of liquid crystal layer, walls, and electrode is often termed a liquid crystal cell. When an electric field is applied between the two electrodes, liquid crystal
10 molecules rotate in the field to an ON state. On removal of the field the molecules rotate back to an OFF state, determined by a surface treatment applied to the walls before cell assembly and by the type of liquid crystal material. The optical transmission characteristics of the ON and OFF states are different. Some
15 devices need one or two polarisers and/or dyes to visibly distinguish between ON and OFF states.

There are broadly three different types of liquid crystal material, nematic, cholesteric, and smectic, each distinguished by a
20 different molecular ordering.

Such materials only show a liquid crystal phase over a limited temperature range between the solid and isotropic liquid phases. Within the liquid crystal phase temperature range a material may exhibit one or more of the nematic, cholesteric or smectic phase
25 types. Normally a material is chosen such that it forms only one type of liquid crystal phase over its working temperature range.

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The present invention concerns devices using smectic liquid crystal materials.

- 5 Displays have been made with the electrodes formed into rows on one wall and columns on the other wall. These collectively form an x, y matrix of separately addressable elements on a large display. One way of addressing such a display is by multiplexing i.e. addressing each row in sequence until the whole display has been addressed. This is repeated all the time that a display is
- 10 needed. Another type of display uses the ON and OFF states to form an electrically switchable optical shutter. Yet another type of display is used as an optical storage device. Nematic cholesteric and smectic liquid crystal material have been used for such devices. A problem with many displays is the time taken to
- 15 switch between the two states i.e. the response times. For many displays a fast response time is needed. A nematic material, arranged in a 90° twisted structure typically has a response time of 100 milliseconds.
- 20 Devices comprising smectic materials have not been used as widely as devices with nematic or cholesteric materials. Available display devices based on smectic materials did not have the necessary characteristics. Recently however ferro electric smectic devices with fast switching and bistability
- 25 characteristics have become of interest. N. A. Clark & S. T. Lagerwall, App. Phys. Letters 36 (11) 1980 pp 899-901. Chiral liquid crystal materials in a tilted smectic phase, e.g. S_C^* , S_I^* , S_F^* , S_J^* , S_G^* , S_H^* are known to exhibit ferroelectric properties. This has been described by R. B. Meyer, L. Liebert, L. Strzelecki
- 30 and P. Keller, J. de Physique (Lett), 36, L-69 (1975).

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According to this invention a method of making a liquid crystal display device comprises the steps;

5 providing two cell walls spaced apart by a spacer to contain a layer of a liquid crystal material, the wall inner surfaces having formed thereon electrode structures and at least one wall surface treated to provide a liquid crystal alignment,

10 providing a tilted chiral smectic liquid crystal material having a cholesteric phase at an elevated temperature above ambient between the chiral smectic and isotropic phases with a cholesteric pitch p greater than half the layer thickness d at a temperature at least 0.1°C above a cholesteric to smectic transition temperature and a significant spontaneous polarization P_s in the chiral smectic phase,

15 heating the mixture to the cholesteric phase, introducing and sealing the mixture into the space between the walls,

20 cooling the material to the tilted chiral smectic phase.

The heating step may be before or after introduction of the material to the space.

25 The liquid crystal material may be a single component or a mixture of components. The material may combine one or more chiral components with laevo (left hand) cholesteric twist sense with one or more chiral components with dextro (right hand) cholesteric twist sense. With such a mixture none of the laevo components can be the racemates of the dextro components. This chiral mixture
30 may be a chiral smectic itself or may be used as an additive to a non-chiral and/or racemate tilted smectic liquid crystal host material. Alternatively the chiral component or components may have the same cholesteric twist sense providing the cholesteric pitch and P_s have the above values.

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The smectic phase has at least one of the following chiral tilted smectic phases C*, I*, F*, J*, G*, K*, H* depending on temperature and may include a smectic A phase between the cholesteric to chiral smectic phase transition.

5

The layer thickness may be up to 15 μm or more, but is typically 1-12 μm , e.g. 2 μm and 6 μm .

10 The p/d ratio is large enough to prevent the material, in its cholesteric phase close to the cholesteric to smectic phase transition, adopting more than a 3π twist, ideally the pitch p is greater than 4d, so that less than π twist can occur in the cholesteric phase near the transition. Ideally this value of p is large over the whole cholesteric phase, preferably is large for 5°C
15 above the smectic/cholesteric transition.

The pitch in the smectic phase is greater than 0.1 μm and preferably much greater, e.g. greater than layer thickness.

20 The value of P_s is at least 0.1 and preferably 1 or more nC/cm^2 . All the chiral components may have substantial values of P_s and the same sense of P_s . Alternatively one or more components may have P_s values of opposite senses providing the net P_s is substantial.

25 For some mixtures the cooling is at a rate of between 0.05° and 2°C /minute within $\pm 5^\circ\text{C}$ of the cholesteric to smectic phase transition. The rate of cooling depends upon the amount of compensation in the cholesteric phase. For well compensated material the cell may be cooled as quickly as is convenient, e.g.
30 20°C/minute or more.

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According to this invention a liquid crystal device comprises a layer of a tilted chiral smectic liquid crystal material contained between two cell walls each carrying electrode structures and at least one wall surface treated to give alignment to the liquid crystal molecules, a first linear polariser and either a second polariser or an amount of dichroic dye in the liquid crystal material,

5 a liquid crystal material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric phase at a higher, above ambient, temperature, with a cholesteric pitch greater than half the layer thickness in the cholesteric phase for at least 0.1°C above the cholesteric to smectic transition temperature, and a substantial spontaneous polarisation.

15 The device cell may be arranged between two polarisers arranged with their optical axes parallel or at a non zero angle to one another. Alternatively the liquid crystal mixture may include an amount of a dichroic dye. In this case only one polariser is needed.

20 The device may further include means for applying two d.c. voltages of opposite polarity to the electrode structures whereby the molecules of the mixture are forced to lie in one of two different positions depending on the polarity of applied voltage and switch between these two positions as the polarity is changed.

25 The cell wall surface treatment may provide similar alignment, in the same or different directions, or different types of alignment, e.g. homogeneous and homoetropic, on the two walls. Alternatively one wall may be left cleaned but with no surface alignment.

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According to this invention a liquid material mixture for use in a tilted chiral smectic liquid crystal device comprises a material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric phase at an elevated temperature, the mixture having a cholesteric pitch greater than $4\text{ }\mu\text{m}$ in the cholesteric phase at least 0.1°C above a cholesteric to smectic transition temperature, and a substantial spontaneous polarisation coefficient P_s , in the smectic phase.

- 10 The device operating temperature typically falls within the range of 0° to 40°C , although for some devices mounted on equipment the upper operating temperature may be about 100°C or even higher.

- 15 Use of chiral components in nematic liquid crystal material is well known. The addition of a chiral component imparts a twist direction to the nematic material director and results in a cholesteric material. The direction of this twist can either be clockwise or anticlockwise, i.e. right or left rotation. Adding two different chiral materials of opposite twist can result in zero
- 20 twist depending upon the composition and temperature of the mixture. Some compounds can have molecules with both right and left rotatory power, these are optical isomers when the optical isomers are present in equal amounts a racemic mixture is formed which is indistinguishable from ordinary non-chiral liquid
- 25 crystalline materials.

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Brief Description of the Drawings

One form of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:-

- 5 Figures 1, 2, are plan and section views of a liquid crystal display device;
- Figures 3, 4, 5, are stylised views of a layer of aligned liquid crystal material showing smectic A, smectic C and smectic C* material respectively;
- 10 Figure 6 is a plan view of a S_C^* cell showing both Ps UP and Ps DOWN molecular alignment states.
- Figures 7(a), (b), (c) are graphs of cholesteric pitch vs temperature for various mixtures;
- Figure 8 is a graph showing variation of half cone angle between UP and
- DOWN states for one material mixture;
- 15 Figure 9 is a graph showing variation of Ps with temperature for one material mixture.

Description of preferred embodiment

- 20 The cell 1 shown in Figures 1, 2 comprises two glass walls, 2, 3, spaced about 1-6 μm apart by a spacer ring 4 and/or distributed spacers. Electrode structures 5, 6 of transparent tin oxide are formed on the inner face of both walls. These electrodes may be of conventional row and column shape or seven segment display. A layer 7 of liquid crystal material is contained between the walls
- 25 2, 3 and spacer ring 4. Polariser 8, 9 are arranged in front of and behind the cell 1. The alignment of the optical axis of each polariser is discussed later. To an approximation the polarisers are crossed and the optical axis of one is nearly parallel or perpendicular to a liquid crystal molecular alignment direction.
- A d.c. voltage source 10 supplies power through control logic 11 to driver circuits 12, 13 connected to the electrode structures 5, 6, by lead wires 14, 15.

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Prior to assembly the walls 2, 3 are surface treated by spinning on a thin layer of polyamide or polyimide, drying and where appropriate curing; then buffing with a soft cloth (e.g. rayon) in a single direction R1, R2. This known treatment provides a

5 surface alignment for liquid crystal molecules. The molecules align themselves along the rubbing direction R1, R2, and at an angle of about 2° to the surface. The directions R1, R2 may in the same or opposition directions. When R1, R2 are arranged in the same direction the contacting liquid crystal molecules tilt

10 towards the layer centre and adapt a splayed configuration across the layer thickness. Surface alignment may be provided by the known process of obliquely evaporating silicon oxide onto the cell walls. As for rubbing alignment the alignment can be parallel in the same or opposite direction. Alternatively one wall may be

15 either left uncoated, or coated with e.g. polyamide and not buffed. Alignment is then provided by the other, rubbed wall surface.

The device may operate in a transmissive or reflective mode. In the former light passing through the device e.g. from a tungsten

20 bulb is selectively transmitted or blocked to form the desired display. In the reflective mode a mirror is placed behind the second polariser 9 to reflect ambient light back through the cell 1 and two polarisers. By making the mirror partly reflecting the device may be operated both in a transmissive and reflective mode.

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Pleochroic dyes may be added to the material 7. In this case only one polariser is needed.

5 An idealised, and somewhat simplistic, arrangement of liquid crystal molecules within a cell is shown diagrammatically in Figures 3, 4, 5. In practice these arrangements may differ considerably from those illustrated, depending in part on cell wall surface effects.

10 Figure 3 shows a layer 7 of smectic A (S_A) material. Axes x, y, z, are used to define directions. The liquid crystal layer lies in x, y plane, layer thickness is in the z direction, rubbing directions R1, R2, are + x, and - x for the upper and lower wall respectively. For an S_A material with these alignments the
15 individual molecules 21 align in the x direction in layers 20 parallel to the y, z plane.

Figure 4 shows a layer of smectic C (S_C) material. Surface alignment is + x and - x as in Figure 3.

20

As in Figure 3 the liquid crystal molecules 21 form into layers 20 parallel to the y, z plane. However S_C molecules 21 adopt a tilted formation within each layer. The tilt is in an x, y plane and at an angle θ to the x axis. Typically θ is 15° - 25°
25 depending on material composition and temperature.

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Figure 5 illustrates smectic pitch in a layer 7 of smectic C* (S_C^*), material. This material forms into layers 20n, with the molecules 21n in each layer lying at an angle 15-25° to the x axis and with this angle 15-25° varying in each layer 21.

- 5 Collectively the molecules form into a twisted structure with the twist axis along the x axis. This is shown in Figure 5 where the molecular alignment in successive layers 21 is shown lying along the surface of a cone with a 45° change between each layer.
- 10 The structure of Figure 5 is termed a tilted chiral smectic phase. Such materials can be produced by the addition of a chiral material to a smectic material. The chiral additive may have either a clockwise or anticlockwise twist, some compounds may have molecules with both senses of twist direction, in which case the material can
- 15 be racemate. Tilted chiral smectic materials can have a spontaneous polarisation and there are two opposing directions for this depending on the configuration of the molecule. In a racemate material the two spontaneous polarisation (Ps) directions are equal and cancel one another and there is no net Ps. With a
- 20 mixture of chiral compounds of opposite twist directions Ps can either be additive or subtractive. Providing there is a net Ps the mixture will exhibit a ferroelectric characteristic.

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One way of producing an aligned S_C^* layer 7 is heating the material into an S_A phase where it is aligned by the cell surface treatment, and then cooling to the S_C^* phase. Unfortunately this cooling can also form the material into a small focal conic structure; a state
 5 with layers of molecules lying in many planes at different angles to one another.

The present invention overcomes this problem by using a material having a cholesteric phase above the smectic phase and providing a
 10 suitable cholesteric pitch as follows:

The material is one having the following phases with increasing temperature;

15 solid - smectic X^* - smectic A - cholesteric - isotropic

solid - smectic X^* - cholesteric - isotropic

where X^* is at least one of the following:- C^* , I^* , F^* , J^* , G^* , K^* ,
 20 H^* . For materials having more than one such smectic phase the phase varies with temperature.

The pitch p in the cholesteric phase is arranged to ensure that the maximum twist across the layer thickness d is not greater than 3π .
 25 A 3π twist can occur when p is about $2/3d$; a 2π twist when p is about d ; a π twist when p is about $2d$; and zero twist when $p > 4d$. Preferably $p > 4d$.

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This cholesteric pitch is necessary for a temperature range of 0.1°C above the smectic/cholesteric transition. Preferably this range is 5°C above the transition and ideally over the entire cholesteric phase.

5

There are a number of ways of achieving the above material. For example combining one or more chiral components with laevo (left) cholesteric twist sense with one or more chiral components with dextro (right) cholesteric twist sense, with the proviso that none of the laevo components are the racemates of the dextro components. Such a mixture may be used by itself if it has the necessary smectic phases. Alternatively the chiral mixture may be added to a non-chiral or a racemate liquid crystal material, eg a smectic C host. Different chiral components may have different temperature/pitch characteristics. In this case it is necessary to ensure that the resultant pitch has the required value in the temperature range above the smectic/cholesteric phase transition.

When using chiral components of opposite twist sense it is necessary to ensure that the resultant mixture has the required spontaneous polarization value P_s . Thus all of the chiral components, regardless of their cholesteric twist sense, may have the same sense of S_C^* polarization, i.e. their P_s add. Alternatively one or more of the chiral components may have the opposite sense of P_s providing the net P_s has a sufficient value.

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Another way of achieving the above material is to use one or more chiral components with the same cholesteric twist sense and S_C^* polarisation sense but still satisfying the cholesteric pitch values noted above. Such a mixture may be used alone or in
5 combination with a non-chiral or a racemate liquid crystal material, eg a S_C host.

As a result of the long pitch in the cholesteric phase the material cools into the S_A phase with uniform alignment caused by the cell
10 wall treatment. The result is alignment as in Figure 3. On further cooling the material adopts the S_C^* phase with alignment approximately as in Figure 6 for mixtures with sufficiently long S_C^* pitch such that the surface alignment unwinds the helical
15 lengths. Materials without an S_A phase are cooled from the cholesteric to a chiral smectic phase. Providing the cholesteric pitch is sufficiently long the cell is well aligned in the S^* phase.

20 The pitch in the tilted smectic phase is arranged to be greater than about $1\text{ }\mu\text{m}$ and preferably very much greater.

The compensation of pitch in the cholesteric phase is illustrated in Figures 7(a), (b), (c). Figure 7(a) shows cholesteric pitch
25 against temperature for a noncompensated material having a cholesteric to smectic transition. At this transition the pitch tends to infinity. The compensated material shown in Figure 7(b) shows a pitch increase to infinity a few degrees above the transition temperature with a pitch reduction below. In Figure 7c
30 the compensation temperature where the pitch goes to infinity occurs just below the smectic to cholesteric transition temperature. By suitable selection of materials this pitch increase can be made to occur even closer to the transition temperature, but a few degrees difference does not seem to affect
35 the end result.

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Some dopants e.g. CC10, CC12 can be used alone in small amounts to give a characteristic shown in Figure 7(c). In this case the material is not compensated as in Figure 7(b) but inherently has a long pitch.

5

When a d.c. pulse of sufficient magnitude is applied to the electrodes 5, 6 the molecules adopt one of two different alignments, D1, D2, depending upon the polarity of the pulse. This is shown in Figure 6 at 21, 22. Note these alignments may not correspond to a zero field alignment. The two molecular directions D1, D2 represent two different Ps directions, i.e. UP and DOWN directions. The polarisers 7, 8 are arranged with their optical axis orthogonal and with the optical axis of one polariser 7 or 8 parallel to direction 21, or 22. Alternatively the polarisers 7, 8 axis may be at non parallel and non orthogonal directions. In each case a different effect is observed in the two switched states.

The cell is observed to change rapidly between a dark and a light state as the d.c. pulses are applied. The angle between directions 21, 22 depends upon the liquid crystal material. Ideally it will be about 45°. Alternatively, when a dye is incorporated into the liquid crystal material, the ideal angle between directions 21, 22 is about 90° with the single polariser aligned along or perpendicular to one of the two directions 21, 22. Figure 8 shows how the angle θ (half the angle between 21, 22) varies with temperature for one material mixture, example 5. The variation of Ps with temperature for this same example 5 is shown in Figure 9.

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The cell 1 may also be used as a shutter when the electrodes 5, 6 are sheet electrodes. Light is blocked or transmitted in the cells of two different switched states. This shutter may also be combined with coloured polarisers to provide a colour switch, arranged in front of a monochrome cathode ray tube (C.R.T.).

A similar arrangement is described in G.B. 1,491,471. In this a C.R.T. emits light in two different wavelengths. The colour switch is switched to transmit the two different colours a frame at a time. This is synchronised to the C.R.T emitting frame sequential images representing the two different colours. Providing the frame time is high enough an observer's eye integrates the two different colour images as one multicolour image.

The present invention provides a colour switch by using a neutral polariser on one side of the cell 1 and two different colour, e.g. red and blue, polarisers on the opposite side the cell. These coloured polarisers are arranged with their optical axis orthogonal. The axis of one coloured polariser is parallel to that of the neutral polariser. The cell is switched at the C.R.T. frame rate as in G.B. 1,491,471.

The cell may also be used as a 90° polarisation switch. In this case the polarisers are arranged with one parallel to the liquid crystal molecules in one of the switched states 21, 22. The second polariser is crossed with respect to the first polariser. The angle between the two directions 21, 22 is about 45°. Providing the birefringence Δn is suitably arranged, of the known expression $\Delta n d / \lambda$, the plane of polarisation of light is rotated by 90°.

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Polarisation switches are useful for example in three dimensional (3-D) television. In this alternate left and right eye frames are displayed. An observer wears polarising glasses and a polarisation switch in front of the TV screen is switched in synchronism with the frame rate. This is described in G.B. 2,062,281 B. A similar effect is obtained if an observer wears glasses that have left and right eye liquid crystal shutters that are switched in synchronism with left and right eye frames on the TV screen.

Examples of materials:-

Chiral Components

	Code		Absolute configuration of chiral groups	Sense of cholesteric twist	Sense of spontaneous polarisation
	CC1	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{COOC}^*\text{H}(\text{Me})\text{C}_6\text{H}_{13}$			
5	CC2	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{COOC}^*\text{H}(\text{Me})\text{C}_6\text{H}_{13}$	R	D	(-)
	CC3	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{COO}-\text{O}-\text{C}_6\text{H}_4-\text{F}-2\text{MB}^*$	S	D	(+)
10	CC4	$2\text{MB}^*-\text{O}-\text{O}-\text{COO}-\text{O}-\text{C}_6\text{H}_4-\text{F}-2\text{MB}^*$	SS	D	(+)
	CC5	$2\text{MB}^*-\text{O}-\text{COO}-\text{O}-2\text{MB}^*$	SS	D	(+)
15	CC6	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{COO}-\text{O}-2\text{MB}^*$	S	D	(+)
	CC7	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{L}^*-\text{O}-\text{L}^*\text{C}_2\text{H}_5$	SS	L	(+)
20	CC8	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{L}^*\text{C}_2\text{H}_5$	S	L	(+)
	CC9	$\text{C}_6\text{H}_{13}-\text{C}^*\text{H}(\text{Me})\text{COO}-\text{O}-\text{O}-\text{COO}-\text{C}^*\text{H}(\text{Me})\text{C}_6\text{H}_{13}$	SS	L	(+)
25	CC10	$\text{C}_9\text{H}_{19}-\text{O}-\text{O}-\text{CO}-\text{C}^*\text{H}(\text{CN})\text{CH}_3$	-	L	(+)
	CC11	$\text{C}_3\text{H}_7-\text{O}-\text{O}-\text{O}-\text{OC}^*\text{H}(\text{Me})\text{CO}_2\text{C}_2\text{H}_5$	-	D	(+)
30	CC12	$\text{C}_9\text{H}_{19}-\text{O}-\text{O}-\text{O}-\text{OC}^*\text{H}(\text{Cl})(\text{Me})\text{CO}_2\text{C}_2\text{H}_5$	-	D	(+)
35	CC13	$\text{C}_8\text{H}_{17}\text{O}-\text{O}-\text{O}-\text{CO}_2-\text{C}^*\text{H}(\text{CN})(\text{Me})\text{CH}_2\text{Me}$	-	D	(+)

where $2\text{MB}^*:-\text{CH}_2\text{C}^*\text{H}(\text{Me})\text{C}_2\text{H}_5$; and $\text{L}^* = -\text{COO}-\text{C}^*\text{H}(\text{Me})\text{COO}-$

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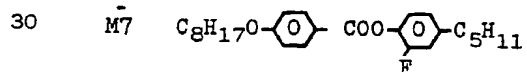
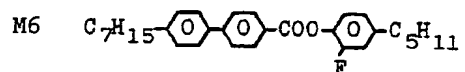
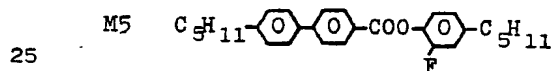
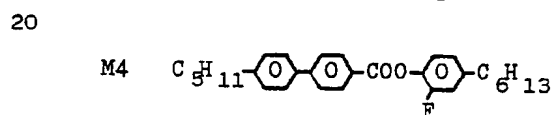
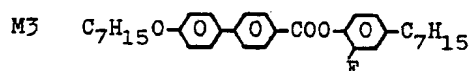
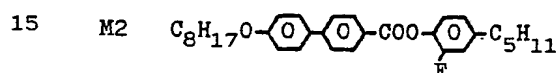
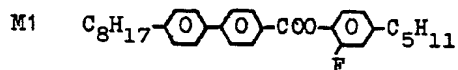
Sense of polarisation according to the convention by S. T. Lagerwall and I Dahl, Mol Cryst. Liq. Cryst. 114 p. 151 (1980).

5 Sense of cholesteric twist and absolute configuration of chiral group convention are described by G. W. Gray & D. G. McDonnell, Mol. Cryst. Liq. Cryst. 34, p.211 (1977):-

D: Dextro

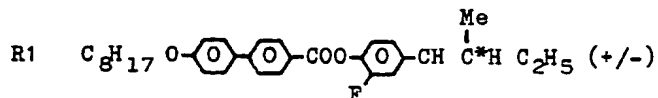
L: Laevo

10 Non-Chiral Materials



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Racemate Materials



5

Sc Host Mixtures

Code	Composition	Transition Temperature °C
H1:-	M1 + M2 + M3 (1 : 1 : 1)	Is 151.7 N 112.7 S _A 107.3 S _C 27.8 S
H2:-	M2 + M3 + R1 (1 : 1 : 1)	
10 H3:-	M1 + M6 + M4 (1 : 1 : 1)	Is N 60 S _C
H4:-	M2 + M3 + M5 (1 : 1 : 1)	Is 155.8 N 89.7 S _C 15 Solid

Key: Is = isotropic, N = nematic, S = smectic, Ch = cholesteric
 Where no subscript is given to a smectic material the particular
 15 phase is unknown.

Example 1:

- (a) 7.9 % R1
 20 (b) 2.2 % CC1
 (c) 90 % M6

This material had the following phases with increasing temperature
 solid - S_C* - S_A - cholesteric - Isotropic.

25

Materials (a), (b) have opposite senses of cholesteric twist, but
 the same sense of S_C* polarization.

When tested in a cell having a 6 μm thick layer excellent alignment
 30 was achieved on cooling down to the S_A and then S_C* phases. When
 tested in a cell with a 12 μm thick layer the mixture showed a pi
 twist in the heated cholesteric phase. Providing the cooling rate
 was slow e.g. about 0.2 °C/min. good alignment was achieved and the
 device could be rapidly switched using the ferroelectric effect.

35

The spontaneous polarization P_s was measured to be about 1nC/square
 cm.

- 20 -

The following Examples 2, 3, 4 use compensated chiral mixtures. These mixtures are composed of chiral components with opposite sense of cholesteric twist, but the same sense of S * spontaneous polarisation.

5

Example 2

CD1:- 23% CC1 + 77% CC3.

This has the phase transition temperature of:-

10 Isotropic 114°C Hol 93.4°C S_A 71.5°C S_C * 50° Solid.

The cholesteric pitch/temperature curve is similar to Figure 7b, the compensation temperature (ie where the pitch is infinite) occurs at ~ 99°C.

15

In a 2 µm cell, a π twist state can be maintained for up to 1°C above the S_A to cholesteric phase transition temperature; with slow cooling good alignment can be achieved in the smectic phases. At 61.5°C the mixture showed a P_s ~ 25 nC/cm² and a tilt angle (i.e. half cone angle) of ~ 18.5°.

20

Example 3

CD3:- 22% CC1 + 78% CC3.

25 This has the following phase transition temperatures:-

Isotropic 115°C Hol 94.6°C S_A 72.6°C S_C * 47° Solid.

The cholesteric pitch/temperature curve is similar to Figure 7b; the compensation temperature (i.e. where the pitch is infinite) occurs at ~ 98°C.

30

In a 2 µm cell, a zero twist state can be obtained, and a π twist can be maintained for up to ~ 6°C above the S_A to cholesteric phase transition temperature.

35

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Example 4

CD9:- 20% CC8 + 80% CC3.

This has the following phase transition temperatures:-

- 5 Isotropic 120.1°C Chol 93.0°C S_A 78.0°C S_C^* 43°C Solid.
The cholesteric pitch/temperature curve is similar to Figure 7b,
the compensation temperature (i.e. where the pitch is infinite)
occurs at $\sim 102^\circ\text{C}$.
- 10 In a 6 μm cell, a 2π twist state can be obtained for up to 0.5°C
above the S_A to cholesteric phase transition.

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Examples 5, 6, 7, 8 use a compensated chiral mixture in an S_C host.

Example 5

CM6 = 43.5% CD3 + 56.5% H1.

5

This has phase-temperature values:-

Isotropic 132.8° Cholesteric 106.8° S_A 83.9° S_C^* 14° S - solid.

10

The pitch/temperature curve is similar to Figure 7b; the mixture being compensated (i.e. infinite pitch) at $\sim 113^\circ\text{C}$. In a $2\mu\text{m}$ and $6\mu\text{m}$ cell, respectively, a zero twist state is obtained for up to 14°C and up to 8°C above the S_A to cholesteric phase transition temperature. Figures 8 and 9 show the tilt angle (ie. half cone angle) and spontaneous polarisation, P_s , as a function of

15

temperature for CM6.

Example 6

CM8 19.6% (49% CC1 + 51% CC4) + 80.4% H1

20

This has phase-temperature values:-

Isotropic 126.1° Cholesteric 84° S_A 65° S_C^* 5° S

25

The pitch/temperature curve is similar to Figure 7b; the mixture being compensated (i.e. infinite pitch) at $\sim 119.5^\circ\text{C}$. In a $2\mu\text{m}$ cell a zero twist state is obtained for a few $^\circ\text{C}$ above the smectic A to cholesteric phase transition temperature.

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Example 7

CM3:- 40% (20% CC1 + 80% CC3) + 60% H3.

This has the following phase transition temperatures:-

5 Isotropic 127.5° Cholesteric 92.4°S_A 72°S_C* 10°S .

The pitch/temperature curve is similar to Figure 7c.

10 In a 6µm cell a zero twist state is obtained for up to 3°C above
the smectic A to cholesteric phase transition temperature.

Example 8

CM11:- 25% CD9 + 75% H4.

15 This has the following phase transition temperatures:-

Isotropic 147.1° Chol 101.1°S_A 85.1°S_C* 13°S .20 The pitch/temperature curve is similar to Figure 7b; the
compensation temperature (i.e. where the pitch is infinite) occurs
at ~ 119°C. In a 2µm cell, a zero twist state can be obtained
just above the smectic A to cholesteric phase transition
temperature.

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Example 9

CM13:- 90% (90% H4 + 10% M7) + 10% (49% CC1 + 51% CC4)

Isotropic 135° Cholesteric 52.3° S_C* -15° S -25° S .

5

In a 6 μ m cell, a 0° twist state was obtained for up to $\sim 10^\circ\text{C}$ above the smectic A to cholesteric phase transition temperature. At 30°C the spontaneous polarisation of the mixture was 3.4 nC/cm² and the tilt angle (i.e. half the cone angle) was 21°.

10

Example 10

CM 15:- 15.9% (31.4% CC9 + 68.6% CC4) + 94.1% H1.

Isotropic 135° Cholesteric 56.1° S_C* 20° Solid.

15

In a 6 μ m cell, a π twist state was maintained for a few degrees Celsius above the smectic C* to Cholesteric transition. The alignment was poor after critically cooling into the S_C* phase, however, by applying ~ 20 Vpk 10Hz square wave, zero twist alignment in the smectic C* could be induced. Heating back up to just into the cholesteric phase and cooling with a d.c. field of appropriate sign then gave the desired alignment.

20

At 50°C and 30°C the spontaneous polarisation of the mixture is 2 nC/cm² and 6.2 nC/cm², respectively.

25

- 25 -

Examples 11, 12 use a single cholesteric twist sense chiral component in an S_C host.

Example 11

5 LPC2:- 1% CC10 + 99% H1.

This mixture has the following phase transition temperatures:-

Isotropic 151° Cholesteric $113.5^\circ S_A$ $104.5^\circ S_C^*$ $28^\circ S$

10 The cholesteric pitch/temperature curve is similar to Figure 7c.

In a $2 \mu m$ cell, a zero twist state can be achieved for $\sim 0.5^\circ C$ above the smectic A to cholesteric transition temperature.

15 The spontaneous polarisation of the mixture is $1.7 nC/cm^2$ and $4.2 nC/cm^2$ at $80^\circ C$ and $40^\circ C$, respectively.

Example 12

20 LPC3:- 1% CC10 + 99% H4.

This mixture has the following phase transition temperatures:-

Isotropic 158° Cholesteric $91^\circ S_A$ $89^\circ S_C^*$ $18^\circ S$ $8^\circ S$.

25 The cholesteric pitch/temperature curve is similar to Figure 7c.

In a $2 \mu m$ cell, a zero twist state can be achieved for $\sim 4^\circ C$ above the smectic A to cholesteric phase transition temperature.

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Example 13

LPC6:- 0.5% CC10 + 99.5% (95% H4 + 5% M7)

Isotropic 152°C Cholesteric 76.8°C S_C^* < 0°C .

5

In a 6 μ m cell, a zero twist state can be achieved for up to 0.2°C above the smectic C^* to cholesteric transition temperature.

Example 14

10

UCM30:- 92.5% (85% H4 + 15% M7) + 7.5% CC12.

The mixture has the following phases -

15 Is 155.8°C Ch 60.5°C S_C^* 15°C.

The cholesteric pitch/temperature curve is similar to Figure 7(c).
 $P_s = 4.4 \text{ nC/cm}^2$ at 50.5°C and 8.4 nC/cm^2 at 25°C. In a 6.2 μ m thick cell a zero twist state can be achieved for $\sim 7^\circ\text{C}$ above the S_C^* to cholesteric phase transition temperature.

20

Example 15

CM20:- 85% H1 + 15% CD18

25

This mixture has the following phases:-

Is 133.7°C Ch 92.8°C S_A 63.2°C S_C^* .

30 In a 2 μ m thick cell a zero twist can be obtained just above the S_A to Ch transition temperature.

$P_s = 18 \text{ nC/cm}^2$ at 25°C.

CD18 = 34% CC1 + 66% CC11

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Example 16

LPM13:- 72.5% H1 + 25% M7 + 2.5% CC13

Is 118° Ch 56.3 Sc* < 0 Solid.

5

 $Ps = 10nC/cm^2$ at 20°C and $5nC/cm^2$ at 46°C.This shows zero twist in a 2 μm cell in the cholesteric phase.

10

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Claims:-

1. A method of making a liquid crystal display device comprises the steps;
providing two cell walls spaced apart by a spacer to contain a layer of a liquid crystal material, the wall inner surfaces having formed thereon electrode structures and at least one wall surface treated to provide a liquid crystal alignment,
providing a tilted chiral smectic liquid crystal material having a cholesteric phase at an elevated temperature above ambient between the chiral smectic and isotropic phases with a cholesteric pitch p greater than half the layer thickness d at a temperature at least 0.1°C above a cholesteric to smectic transition temperature and a significant spontaneous polarization P_s in the chiral smectic phase,
heating the mixture to the cholesteric phase,
introducing and sealing the mixture into the space between the walls,
cooling the material to the tilted chiral smectic phase.
2. The method of claim 1 and comprising the further steps of reheating to above the smectic/cholesteric transition temperature and slowly cooling, whilst a unidirectional voltage pulse is applied.
3. The method of claim 1 wherein the material is cooled at a rate of less than $20^{\circ}\text{C}/\text{minute}$ within $\pm 5^{\circ}\text{C}$ of the cholesteric/smectic phase transition.
4. The method of claim 1 wherein the material is cooled at a rate of less than $2^{\circ}\text{C}/\text{minute}$ within $\pm 5^{\circ}\text{C}$ of the cholesteric/smectic phase transition.

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5. The method of claim 1 wherein both walls are surface alignment treated and the cell is arranged with the alignment direction parallel in the same direction.
- 5 6. The method of claim 1 wherein both walls are surface alignment treated and the cell is arranged with the alignment direction parallel in opposite directions.
7. The method of claim 1 wherein the alignment is produced
10 by unidirectional rubbing.
8. The method of claim 1 wherein the alignment is produced by oblique evaporation of silicon oxide.
- 15 9. A liquid crystal device comprising a layer of a tilted chiral smectic liquid crystal material contained between two cell walls each carrying electrode structures and at least one wall surface treated to give alignment to the liquid crystal molecules, a first linear polariser and either a second polariser or an amount
20 of dichroic dye in the liquid crystal material, the liquid crystal material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric phase at a higher, above ambient, temperature, with a cholesteric pitch greater than half the layer thickness d in the cholesteric phase
25 for at least 0.1°C above the cholesteric to smectic transition temperature, and a substantial spontaneous polarisation.
10. The device of claim 9 wherein the cell walls are surface
30 treated to align liquid crystal molecules in the same direction with a splayed configuration across the layer thickness.

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11. The device of claim 9 wherein the electrodes are formed as strip electrodes arranged in a matrix format.
12. The device of claim 9 wherein the electrodes are formed as strip electrodes arranged in a segment format.
13. The device of claim 9 wherein the electrodes are formed as sheet electrodes.
14. The device of claim 9 wherein the liquid crystal layer thickness is up to 15 μm .
15. The device of claim 9 wherein the cholesteric pitch p is greater than $d/2$ at a temperature at least 5°C above the transition temperature.
16. The device of claim 9 wherein one polariser is a neutral polariser and the second polariser is replaced by two differently coloured polarisers arranged with their optical axis orthogonal.
17. The device of claim 9 wherein one polariser is arranged with its optical axis parallel to the liquid crystal molecular alignment in one of its switched states, and the other polariser is arranged with its optical axis crossed with respect to the first polariser.
18. The device of claim 9 wherein the cholesteric pitch within 0.1°C of the cholesteric/smectic transition is greater than four times the liquid crystal layer thickness.
19. The device of claim 9 and further comprising means for applying the two d.c. voltages of opposite polarity to the electrode structures to switch the liquid crystal material into its two different states.

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20. A liquid crystal material mixture for use in the method of claim 1 comprising a material having a tilted chiral smectic phase at normal device operating temperatures and a cholesteric phase at an elevated temperature, the mixture having a cholesteric pitch greater than $4\text{ }\mu\text{m}$ in the cholesteric phase at least 0.1°C above a cholesteric to smectic transition temperature, and a substantial spontaneous polarisation coefficient P_s , in the smectic phase.
21. The material of claim 20 wherein the material has the following phases with temperature:-
isotropic \rightleftharpoons cholesteric \rightleftharpoons smectic A \rightleftharpoons chiral smectic \rightleftharpoons solid.
22. The material of claim 20 wherein the material has the following phases with temperature:-
isotropic \rightleftharpoons cholesteric \rightleftharpoons chiral smectic \rightleftharpoons solid.
23. The material of claim 20 wherein the pitch in the cholesteric phase is greater than $4\text{ }\mu\text{m}$ over a temperature range up to 5°C above the cholesteric smectic phase transition.
24. The material of claim 20 wherein the smectic pitch is greater than $2\text{ }\mu\text{m}$.
25. The material of claim 20 wherein the spontaneous polarisation is greater than 0.1 nC/cm^2 .
26. The material of claim 20 wherein the cholesteric/smectic phase transition is above 40°C .
27. The material of claim 20 wherein the cholesteric smectic phase transition is above 100°C .
28. The material of claim 20 and further including an amount of a dichroic dye.

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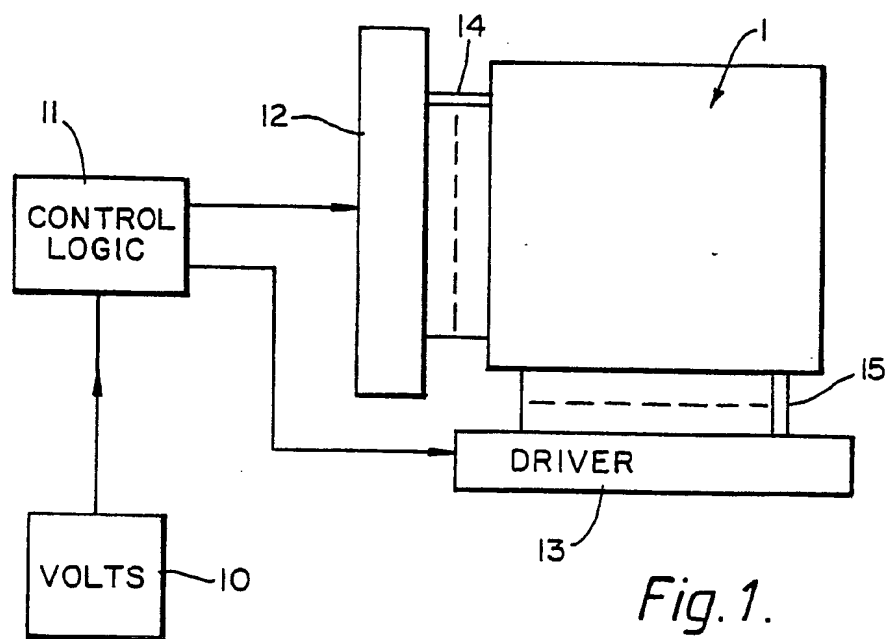


Fig. 1.

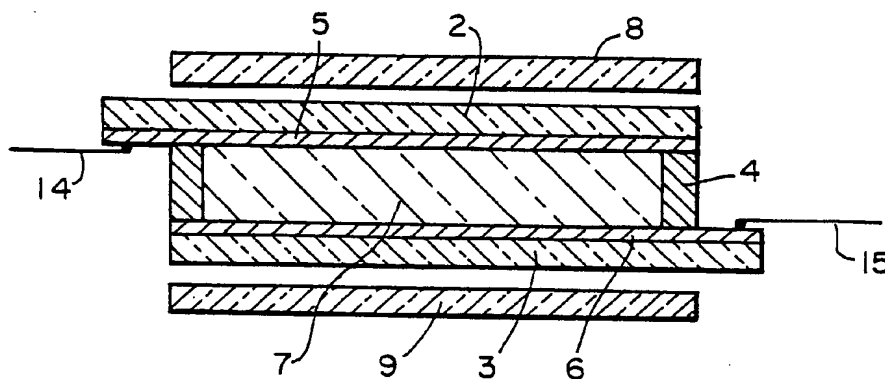


Fig. 2.

Fig.3.

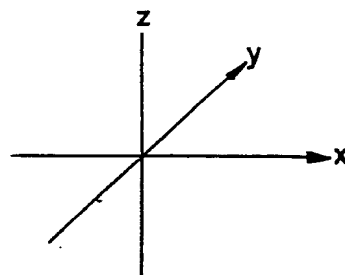
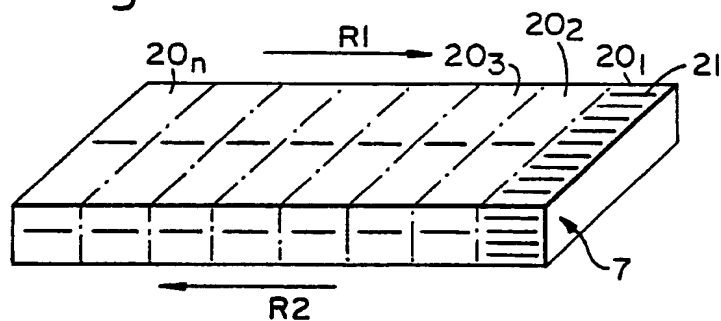


Fig.4.

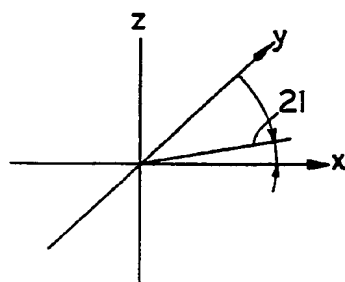
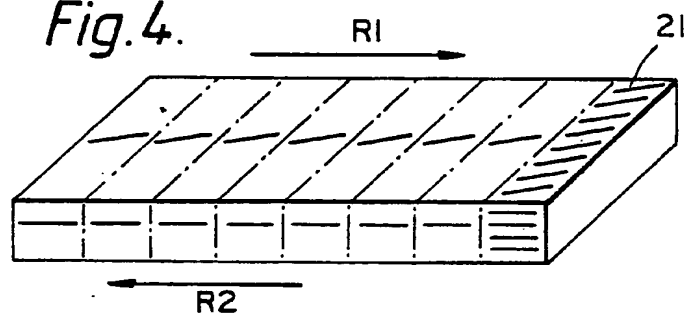
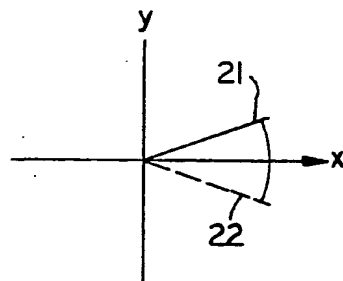
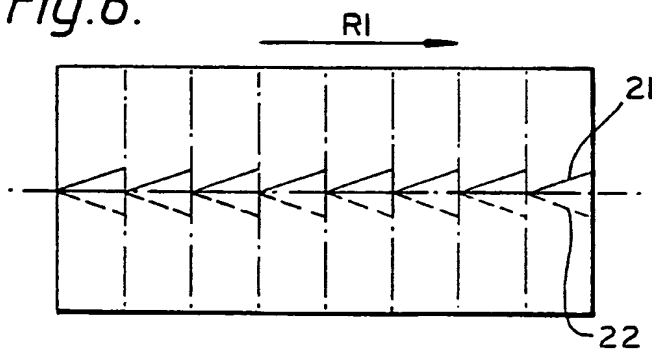
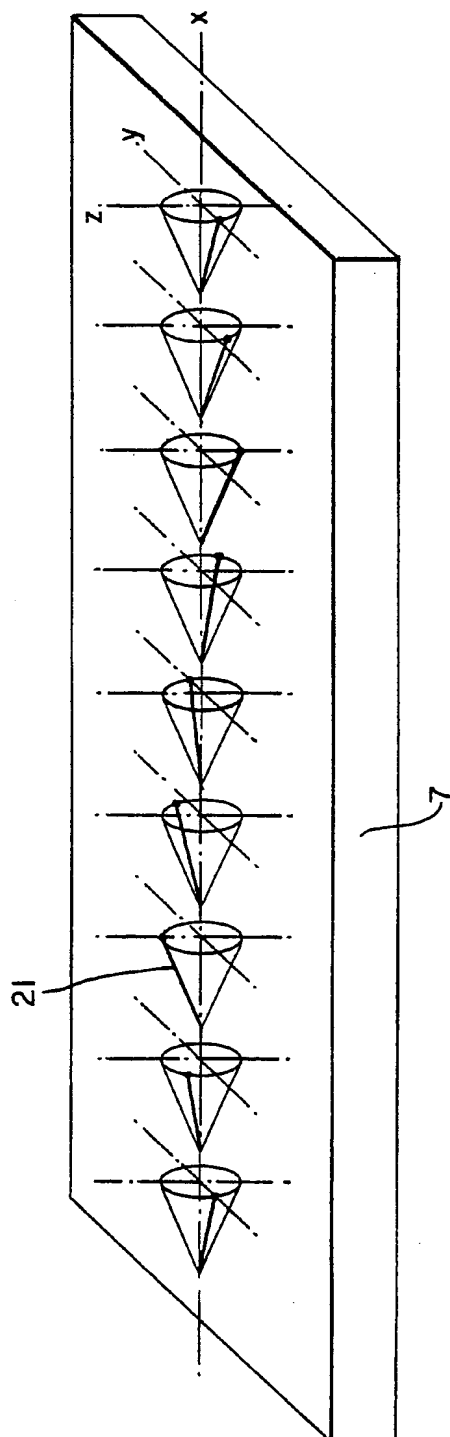


Fig.6.

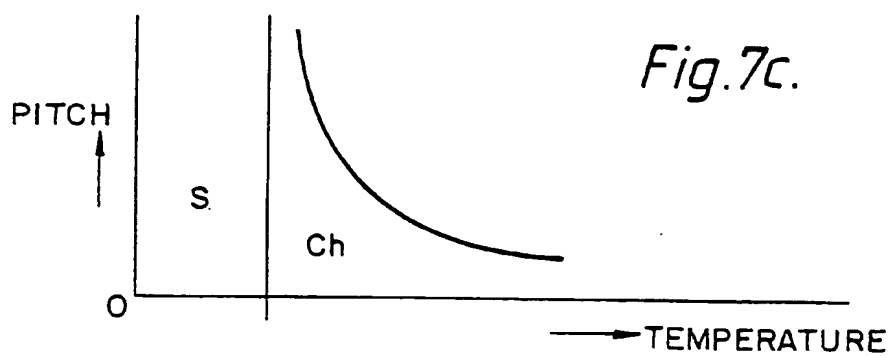
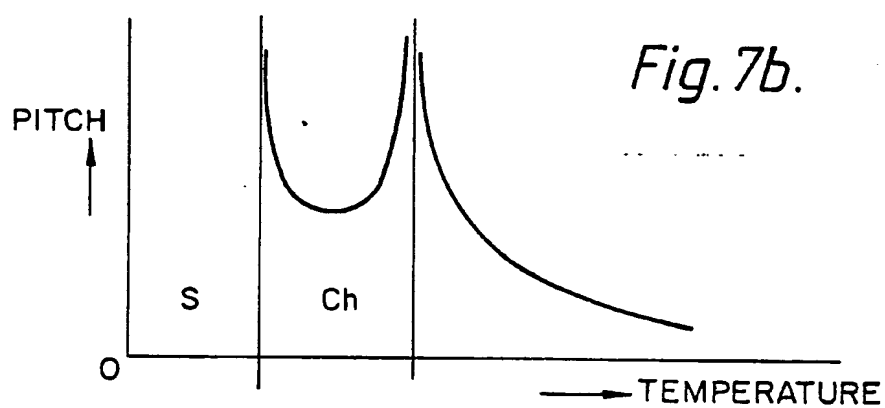
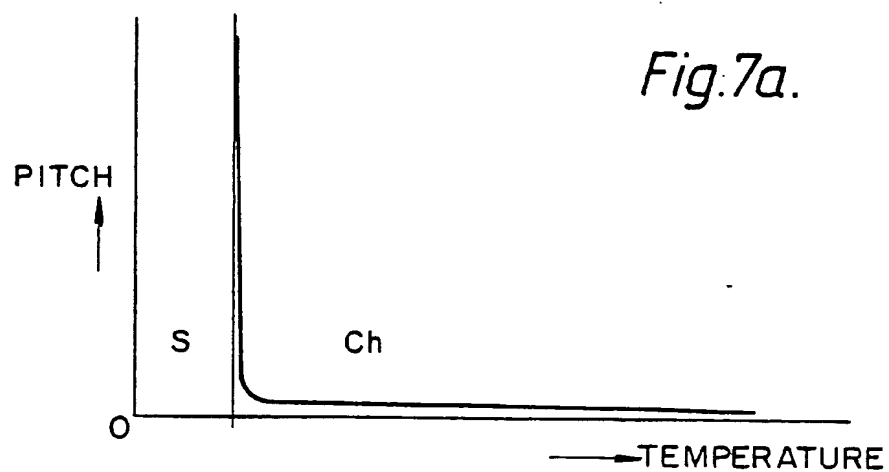


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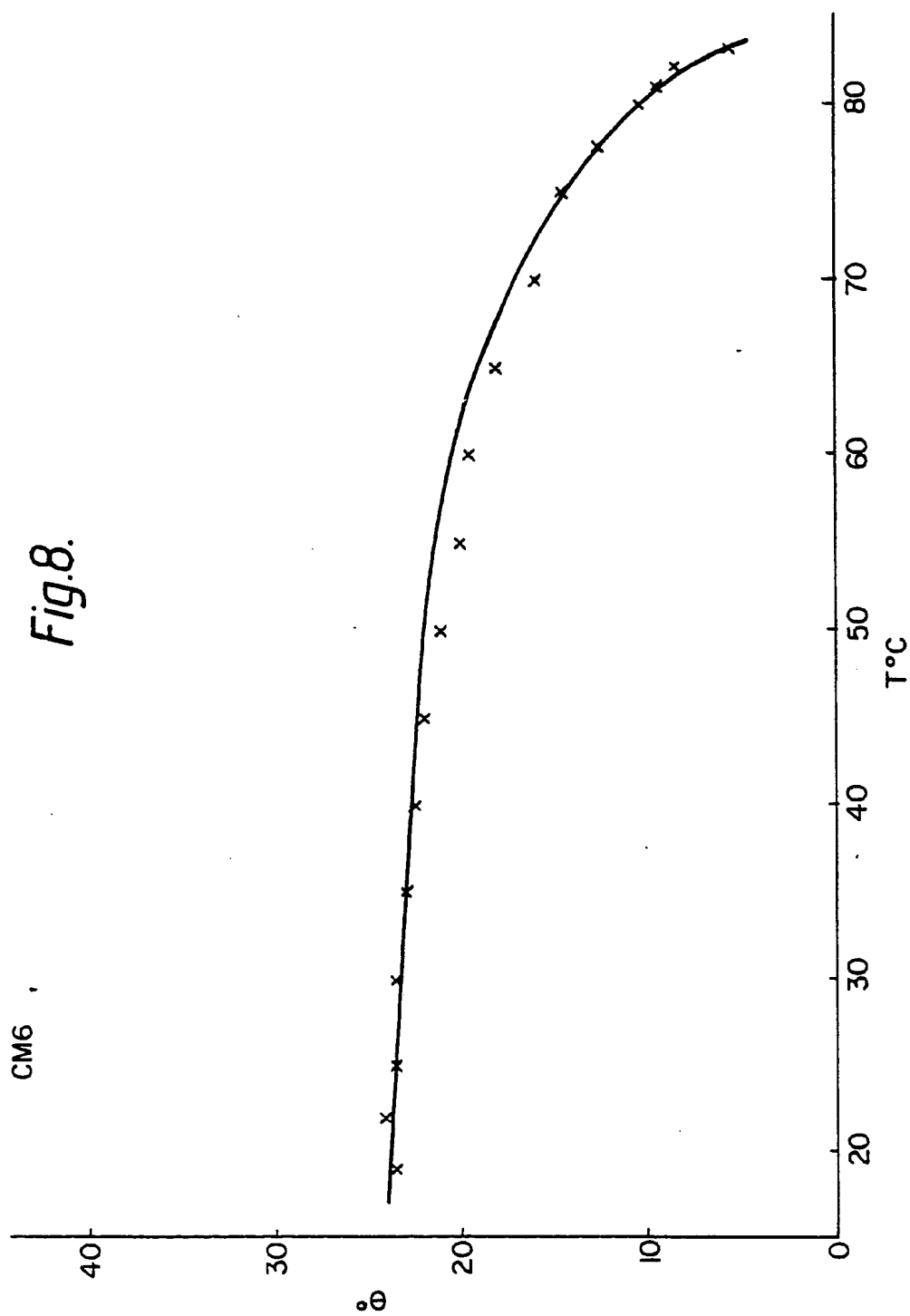
Fig.5.



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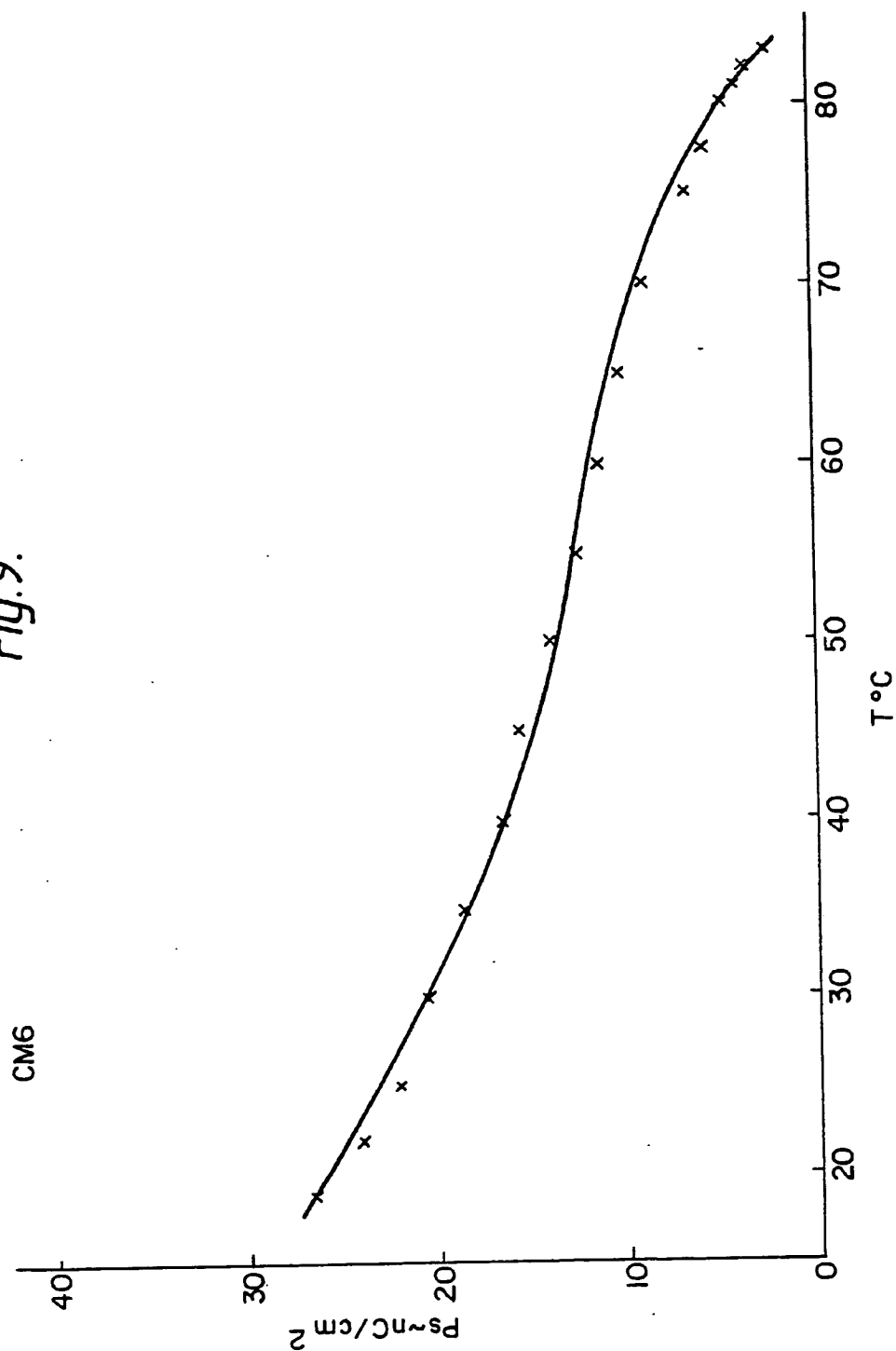


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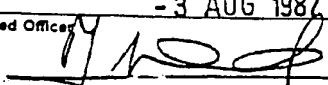
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Fig. 9.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00222

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : G 02 F 1/137		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
IPC ⁴	G 02 F 1/00; C 09 K 19/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
A	FR, A, 2567533 (CANON K.K.) 17 January 1986 see page 12, line 20 - page 13, line 34; page 20, lines 13-29	1,5-9,11, 20-22
A	EP, A, 0136725 (CHISSO CORP.) 10 April 1985 see page 1, lines 1-9; page 4, line 9 - page 5, line 23; page 8, lines 6-17; page 14, line 15 - page 15, line 4	1,9,20,25, 28
A	EP, A, 0149398 (THOMSON CSF) 24 July 1985 see page 6, lines 6-29; page 8, lines 1-6	1,19
A	EP, A, 0138006 (MERCK GmbH) 24 April 1985 see page 2, line 5 - page 3, line 19; page 6, lines 10-21	1
A	Applied Physics Letters, volume 47, no. 12, 15 December 1985, American Institute of Physics, (Woodbury, New York, US), J.S. Patel: "Room-temperature switching behavior of ferroelectric liquid crystals in thin cells", -/.	
<p>* Special categories of cited documents: 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2nd July 1987	- 3 AUG 1987	
International Searching Authority	Signature of Authorized Officer	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
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A	EP, A, 0091637 (HITACHI LTD) 19 October 1983 see page 35, line 18 - page 36, line 21	2,9
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A	EP, A, 0092181 (HITACHI LTD) 26 October 1983 see page 3, lines 1-24; page 7, line 16 - page 8, line 17	9
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A	Electronics International, volume 56, no. 10, May 1983, (New York, US), C. Barney: "Fast LC switch handles color", pages 52,54 see the whole document	16
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A	Molecular Cystals & Liquid Crystals, volume 110, 1984, Gordon and Breach, Science Publishers, Inc., (New York, US), J.W. Goodby et al.: "Ferroelectric liquid crystals - structure and design", pages 175-203 see pages 180-181, chapter 1.2.: Compensated helical phases"; page 184, lines 4-10; page 201, chapter 3.3	1,20-22,28
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 87/00222 (SA 16708)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/07/87

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		JP-A- 61103124	21/05/86

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